ETHANOL: VAPOR PHASE CATALYST STUDIES

BY

LLOYD RICHARD MICHELS

B. S., University of California, 1938

M. S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS
1941

ETHANOL: VAPOR PHASE CATALYST STUDIES

BY

LLOYD RICHARD MICHELS

B. S., University of California, 1938

M. S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS

1941

ACKNOWLEDGMENT

The author wishes to express his deep appreciation to Dr. Donald B. Keyes, under whose direction this thesis was prepared and to Dr. Sherlock Swann, Jr., for their many helpful suggestions throughout this investigation.

ETHANOL: VAPOR PHASE CATALYST STUDIES

Introduction

The study of the catalytic vapor-phase oxidation of ethyl alcohol has been the subject of numerous investigations during the past century. Data on the ethanol oxidation is of value both from the standpoint of the theory involved and the economic importance of the oxidation products.

This investigation was undertaken with the view of determining the effects produced by changing the variables in the ethanol oxidation system one at a time and of formulating the mechanism of the ethanol oxidation by studying the oxidation of the alcohol intermediates.

Experimental

The liquid reactants were vaporized into an air stream, the liquids having been fed to the vaporizer by small bellows pumps of special construction. The resulting vapor mixture was passed over the heated catalyst and the liquid products formed were separated from the gas stream by condensation in ice and dry-ice-acetone traps and by scrubbing with ice water.

The catalyst chamber was identical with that used by Foster[1], a catalyst volume of 21.6 cc. being used in all cases, and the catalyst temperature being measured at a point 13/16 inches from the top of the catalyst bed. In order to control the catalyst temperature accurately, the converter was placed in a high temperature thermostat.

In formulating the mechanism of the ethanol oxidation, a single platinized silica aerogel was employed, the catalyst having been prepared by Kearby[2]. Two other catalysts were used in later work, one a plain silica aerogel and the other a different platinized aerogel, both catalysts however being made according to the directions given by Kearby, with the only change being in the platinum content.

The exit gases were analyzed for carbon dioxide, oxygen, ethylene, carbon monoxide, hydrogen, methane, and ethane with the U. S. Bureau of Mines Apparatus. The liquid products were analyzed for acid by titration with base, for ester by hydrolysis

in base followed by hydrolysis in acid, and for aldehyde using a modification of the Ripper[3] method, in which bisulfite solutions were titrated into standard iodine solutions.

Results and Conclusions

1. A maximum conversion of alcohol to acetaldehyde of 54% was obtained with Kearby's platinized aerogel at a temperature of 280° C. using an alcohol rate of 0.216 cc./min. and an air velocity of 0.0215 cu. ft./min.; acid yields were never greater than three percent. The plain aerogel when tested under identical conditions indicated a conversion to acetaldehyde of 25% accompanied by a 22% conversion to acetic acid at a catalyst temperature of approximately 270°C.
2. A definite ratio of air to alcohol is required for maximum conversion to acetaldehyde using a platinized aerogel catalyst. This ratio increases with increasing space velocity.
3. Conversion of alcohol to acetaldehyde increases almost linearly with decreasing space velocities.
4. At a constant space velocity and air to alcohol ratio, the conversion to acetaldehydes attains a maximum at a definite catalyst temperature. Above this temperature conversions to aldehyde decrease while conversions to carbon dioxide and total conversions increase.
5. Under the mose favorable conditions in the normal ethanol "oxidation," dehydrogenation can account for but fifteen percent of the acetaldehyde formed.
6. Water has little effect in the ethanol oxidation other than that of increasing the space velocity and thereby decreasing slightly the conversions to acetaldehyde and carbon dioxide.
7. The effect of acetic acid in the oxidation of alcohol is similar to that of water, conversions to aldehyde decreasing due to an increase in the space velocity.
8. In the oxidation of acetaldehyde total conversions and conversions to acetic acid fall off sharply at high catalyst temperatures.
9. At low catalyst temperatures in the acetaldehyde oxidation, water tends to decrease slightly the conversion to acid and

the decomposition into carbon monoxide and methane, but inhibits markedly the oxidation into carbon dioxide and water.

10. At high catalyst temperatures in the acetaldehyde oxidation, water has a quite different effect, increasing rather than decreasing the oxidation to carbon dioxide and water and the decomposition into carbon monoxide and methane while decreasing the already small acid conversion.
11. At low catalyst temperatures alcohol inhibits markedly the oxidation of acetaldehyde to acetic acid and carbon dioxide, the inhibition being due to a blanketing of the catalyst surface by alcohol molecules; at high catalyst temperatures not only does alcohol fail to inhibit the acetaldehyde oxidation but is itself oxidized to acetaldehyde.
12. Platinized silica aerogel catalyzes the oxidation of acetic acid into carbon dioxide and water, the reaction being favored by high air to acid ratios and high catalyst temperatures.
13. Platinized silica aerogel also catalyzes to some extent the oxidation of carbon monoxide to carbon dioxide and the reduction of carbon monoxide by hydrogen to saturated hydrocarbons.
14. Low acid yields in the ethanol oxidation are due in most part to the fact that the acetaldehyde which has been formed at high temperature is not adsorbed strongly enough by the catalyst to enter into further reaction.
15. In the ethanol oxidation, carbon dioxide is a primary oxidation product of both ethyl alcohol and acetaldehyde and is formed to a slight extent by oxidation of the acetic acid formed.
16. In the ethanol oxidation, the conversion to carbon dioxide may be decreased by using high alcohol to air ratios, lower catalyst temperatures, or by adding water; in the acetaldehyde oxidation carbon dioxide formation may be minimized by using lower catalyst temperatures and adding either water in large amounts or alcohol in minute quantities.
17. The effect of platinum in platinized silica aerogels is to increase the conversion to acetaldehyde and carbon dioxide

and the conversion of oxygen and to decrease the conversion to acetic acid, ethyl acetate, hydrogen, and carbon monoxide.

18. The kinetics of the alcohol oxidation cannot be explained on the basis of molecular collisions alone; indeed it is apparent that the oxidation mechanism is a function of many variables and cannot be accounted for by any general theory yet devised.

References

[1]. Foster, H. D. and Keyes, D. B., Ind. Eng. Chem., 29, 1245, (1937).

[2]. Kearby, K. K., Ph.D. Thesis, University of Illinois, (1937).

[3]. Ripper, M., Monatsch. 21, 1079, (1900).

VITA

The author was born in San Francisco, California on August 2, 1916. He received both his primary and secondary education in the San Francisco public schools, graduating from Lowell High School in 1934. He received the degree of Bachlor of Science in Chemistry from the University of California in 1938 and the degree Master of Science from the University of Illinois in 1940. He served as an Assistant in Chemical Engineering at the University of Illinois from September, 1939 until June, 1941.

The author is a member of Pi Mu Epsilon, Phi Lambda Upsilon, and Sigma Xi.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0039